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A calculation of activation energy of hydrogen diffusion in alkali halide crystals

C NEOGY AND S K DEB

Department of Physics, University of Kalyani, Kalyani

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Taking a semi-continuum model, we have calculated the activation energy of atomic and molecular hydrogen diffusion in NaCl and KCl crystals, by minimising the total change of energy of the lattice when the defect occupies an interstitial position. The contributions from electrostatic, polarisation and repulsive energy are considered.

1 INTRODUCTION

Hydrogen can diffuse in alkali halides either in the atomic or in the molecular form. The activation energy for molecular hydrogen diffusion in potassium halides has been determined experimentally by Grundig & Ruhenbeck (1972). Hirai (1960), Diaz-Gongora & Ruiz-Mejia (1973) have also shown the existence of H_2 molecules in alkali halides. Hydrogen atom in an ionic crystal can come from a defect U_9-centre in an anion site which transforms ultimately to a F-centre in an anion site and a neutral H-atom in an interstitial position. A paramagnetic resonance experiment by Delbecq *et al* (1956) shows that under the proper conditions H atoms are stable products in a photo decomposition of a U-centre. These H atoms are very mobile and even at 120°K, the diffusion of H atoms to form molecules are so rapid, that no signal due to H atoms are observed. But, according to Hall & Schumacher (1962), who has obtained densities of interstitial atomic hydrogen as high as $10^{19}/cm^3$. H atoms remain within the interstitial space very much like a free atom. Thus it seems mechanism for production of hydrogen interstitial atoms within the crystal is not completely known. To understand the exact mechanism of hydrogen diffusion in ionic crystals, experiments are being done in our laboratory. So we think it worthwhile to calculate theoretically the activation energy of such diffusion. The diffusion of hydrogen can be calculated assuming the gas entering the crystal as a neutral atom or as a neutral molecule occupying an interstitial position and that the concentration is sufficiently low so that gas-gas interactions in the solid can be neglected. By comparing the calculated and the experimental activation energies of such hydrogen diffusion, one can infer about the nature of the defect—whether it is a hydrogen atom or a hydrogen molecule.

2 Method of Calculation

We place the defect atom in two positions—once in a square centre position (S position) and then in a cube centre position (C position) (as shown in the figure) In each position, we calculate the change in the lattice energy (as a result of introduction of the defect atom) as a function of the radial relaxation (σ) of the

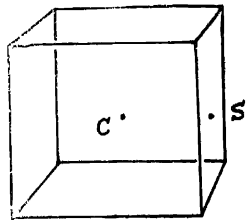

Figure 1. Positions of square centre (s) and cube centre (c)

nearest movable ions In the square centre position, we have relaxed the nearest four ions and in the cube centre position, eight nearest neighbour ions are relaxed We assume the amount of relaxation to be the same for both the type of ions which is an approximation only Our defect calculation includes (i) electrostatic contribution ΔE_{ES} from all the host ions, (ii) polarisation energy contribution ΔE_{POL} as a result of the displacement of ionic charges from their normal positions giving displacement dipoles and considering the contribution from all the ions on the first sixteen neighbouring shells and (iii) repulsive contributions between the host ions themselves and also between the host ions and the defect atom As repulsive energy is a very short range energy, we consider the contribution from the first five nearest neighbour shells The properties of the defect atom directly enters only in the repulsive term and in the other two energy terms—through the relaxation that it produces Therefore, we actually calculate,

$$\Delta E_{Total}\ (\sigma) = \Delta E_{ES}\ (\sigma) + \Delta E_{POL}\ (\sigma) + \Delta E_{REP}\ (\sigma)$$

where σ is the change per unit length

We calculate the value of ΔE_{Total} for different values of σ and find that for some values of σ ΔE_{Total} has its minimum value for both the C and S positions Physically this means thus σ gives the amount of radial displacement of the ions in the nearest shell when the defect atom occupies sites C and S The difference of the minimum of the ΔE_{Total} between those C and S positions gives the activation energy of the defect diffusion

3. Electrostatic Energy

We will recognise the movable ions by the subscript i and j and by k we will mean those ions which are unrelaxed. Another subscript l is used for all ions in general The number of movable ions (denoted by M) in the square

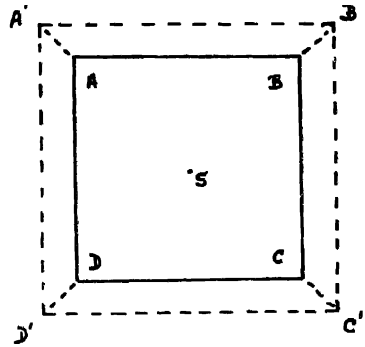

Figure 2. Normal and relaxed positions of nearest neighbour ions around square centre positron

centre case is four and in the cube centre case it is eight When the defect atom occupies position S, the four ions at A B, C, D are relaxed to A', B', C', D' We define

$$\Delta E_{ES} = \text{Change in electrostatic energy of the lattice}$$
$$= E_1 - E_2 + E_3$$

where,

$$E_1 = M \times Z_l \sum_{l \neq i}^{\infty} \left[\frac{Z^l}{|r'_l - r_l|} - \frac{Z_l}{|r_l - r_l|} \right]$$

= (No of movable ions) × (change in electrostatic energy when A is displaced to A' but all other ions are at normal lattice sites)

In E_1, we calculate the electrostatic energy change when A is displaced to A' but all other ions are undisplaced—but actually when A is displaced to A', B, C and D are also displaced to B', C' and D' Therefore, we subtract E_2 from E_1 and add E_3 to that, where

$$E_2 = M \times Z_l \sum_{j \neq 1}^{M} \left[\frac{Z_j}{|r'_l - r_j|} - \frac{Z_j}{|r_l - r_j|} \right]$$

and

$$E_3 = \tfrac{1}{2} M \times Z_l \sum_{j \neq 1}^{M} \left[\frac{Z_j}{|r_l' - r_j'|} - \frac{Z_j}{|r_l - r_j|} \right]$$

E_2 and E_3 can be calculated numerically term by term But E_1 is calculated from the following relation—

$$V = \frac{e}{r_0} [\alpha_M + 3\ 7(x^4+y^4+z^4) - 10\ 8(x^2y^2+y^2z^2+z^2x^2)] \quad \ldots \quad (1)$$

where α_M is the Madelung constant and V is the electrostatic potential at (x, y, z) near an ion site $(0, 0, 0)$ assuming the ion at $(0, 0, 0)$ missing (Hatcher & Dienes 1961)

4 Polarisation Energy

We have assumed the ions are polarisable and the polarisation energy results from the energy of formation of a dipole and its interaction with the electric field at that lattice site

$$\Delta E_{POL} = -\tfrac{1}{2} \sum_{l}^{\infty} \alpha_l E_l^2$$

where α_l = polarizability of an ion, and E_l = electric field that it experiences

To calculate the polarisation energy, we divide the lattice into two parts—an inner region comprising of the movable ions and an external region containing the rest of the lattice

Therefore, $$\Delta E_{POL} = \Delta E_{P_1} + \Delta E_{P_2}$$

Let E be the field corresponding to the potential V of eq (1)

Then,

E_l = field at the lattice site of the lth ion

$$= E - \sum_{j \neq l}^{M} \frac{Z_j(r'_l - r_j)}{(|r'_l - r_j|)^3} + \sum_{j \neq i}^{M} \frac{Z_j(r'_l - r'_j)}{(|r'_l - r'_j|)^3}$$

and

$$\Delta E_{P_1} = \tfrac{1}{2} \sum_{l}^{M} \alpha_l E_l^2$$

We next proceed to find the change in polarisation energy from all the undisplaced ions Though in this second region ions are assumed unrelaxed, still as a result of the movable ions, a field is experienced by all the other ions of the lattice Here again an infinite lattice sum is required, but we calculate the contribution from all the ions in the first sixteen neighbouring shells

$$E_k = -\sum_{l=1}^{M} \frac{Z_l(r_l - r_k)}{(|r_l - r_k|)^3} + \sum_{l=1}^{M} \frac{Z_l(r'_l - r_k)}{(|r'_l - r_k|)^3}$$

and

$$\Delta E_{P_2} = -\tfrac{1}{2} \sum_{k} \alpha_k E_k^2$$

the sum over k extends over all ions in first sixteen neighbouring shells.

5 Repulsive Energy

Of all these three energy terms, the least certain term is the repulsive energy between the defect atom and the host ions. The repulsive energy between the host ions are well given by an empirical relation by Born & Mayer (1932) But this type of potential (i.e., exponential) was proposed mainly for the interacting ions at normal lattice sites, i e , when the ions are near their equilibrium separations. When a defect atom is placed in an interstitial position, the distance between the defect atom and the host ions is very close and relatively little is known about these repulsive potentials at such smaller separations. Various other potentials to take account of these type of interactions are also proposed (Abrahamson *et al* 1961) The ordinary repulsive parameters of Born-Mayer potential b and ρ have been obtained empirically from various static crystal data Many workers have used the same potential for finding the repulsive energy between an ion and a neutral defect atom (Norgett & Lidiard 1968). We have also used the same b and ρ values for the interaction between the defect atom and the host ions as is used for the interaction between two host ions At present there is no better method of finding this repulsive energy A recent work by Deb & Ghosh (1975) has shown, that those b and ρ values can be correlated to the overlap charge densities and the overlap separations of the interacting ions at the normal lattice sites Without further modification, this method as such cannot be applied for an interstitial defect However, it will be very interesting, to find the repulsive interaction parameters between a defect atom and a host ion, according to this principle and this will be applied in our next paper

The repulsive energy between the two ions is given by.

$$E_{REP}(r_{ij}) = bC_{ij}\exp\{(r_i+r_j-r_{ij})/\rho\}$$

where C_{ij} is the Pauling factor

$$= 1 + \frac{Z_i}{N_i} + \frac{Z_j}{N_j}$$

where Z_i Z_j are the charges of the ions, N_i, N_j are the number of electrons in the outermost shells r_i, r_j are the ionic radii and b and ρ are two values obtained empirically.

The total change in the repulsive energy is divided into two parts,

$$\Delta E_{REP} = \Delta E_{r_1} + \Delta E_{r_2}$$

The first part gives the change in the repulsive energy due to all the host ions among themselves The second part gives the change in the repulsive energy that arises from the interaction of the defect atom with the host ions As

repulsive energy is a short range energy, we have considered contribution from the first five neighbouring shells.

$$\Delta E_{r_1} = \tfrac{1}{2}\sum_{i}^{M}\sum_{j}^{M}[E_r(|r_i' - r_j'|) - E_r(|r_i - r_j|)] + \sum_{i}^{M}\sum_{K>M}[E_r(|r_i' - r_k|) - E_r(|r_i - r_K|)]$$

and

$$\Delta E_{r_2} = \sum_{i}^{M}[E_r(|r_D - r_i'|)] + \sum_{K}[E_r(|r_D - r_K|)]$$

where r_D is the coordinate of the defect atoms

6 Calculations

A computer program of all these above formulae is done and results are obtained from IBM 1130 The following input data is taken from Chaudhury *et al* (1975), which have been determined from extrapolated 0°K values of the most recent elastic constant and density measurements of alkali halides

Table 1 All values are in a u

Lattice	r_+	r_-	r_0	b	ρ
NaCl	2.267	3.061	5.271	0 00497	0.577
KCl	2.853	3.08	5.872	0 00408	0.556

The electronic polarisabilities of the ions were taken from Tessmann *et al* (1953) The radius of the defect H atom was taken to be 0·529Å and that of the hydrogen molecule was taken to be 2·2117 a u (Hirschfelder *et al* 1967)

A minimum in the total change in energy ΔE_{Total} as a function of the radial relaxation was obtained for both the square centre and the cube centre positions The calculations were done for two different host lattices—sodium chloride and potassium chloride

A portion of the actual calculation showing contribution from the various energy terms is given in table 2

The final values of both the systems is shown in table 3.

From the detailed calculation, it is seen that as the diameter of the interstitial defect increases the amount of relaxation also increases. The activation energy also increases as the defect size increases On the other hand the activation energy for H atom in NaCl lattice is greater than that in KCl (whose interionic separation is larger), but for H_2 molecule the case is reversed

Comparison of those calculated values with the existing experimental values are not straightforward The activation energy of H_2 diffusion in KCl as given by Grundig & Ruhenbeck (1972) is 0·96 ev Our calculated values are 0 48 ev.

Table 2 All energies are in a u NaCl Lattice

σ	ΔE_{ES}	ΔE_{POL}	ΔE_{REP}	ΔE_{Total}
	H Atom in the Cube Centre position			
0.010	−0.00028	−0.00013	0 00860	0 00901
0 012	−0.00037	−0 00017	0.00814	0.00898
0 014	−0 00017	−0.00021	0.00829	0.00897
0.015	−0.00057	−0.00026	0.00813	0 00898
0.017	−0 00069	−0.00032	0 00799	0 00900
0.035	−0 00247	−0.00115	0 00635	0 00997
	H Atom in the square centre position			
0 042	−0.00143	−0.00084	0 01401	0 01628
0 056	−0 00248	−0.00148	0.01202	0.01598
0 071	−0.00397	−0.00230	0 01011	0.01621
0 085	−0 00529	−0.00329	0 00834	0 01692

This is much less than the experimental values—but if there remains a large number of vacancy complexes, then the experimental values will be higher, because part of this energy goes to lift the defect out of the vacancy complex

Table 3 All energies are in a u

Nature of the defect	Position *C*		Position *S*		Activation energy
	E_{MIN}	Relaxation	E_{MIN}	Relaxation	
	NaCl crystal				
H atom	0 00897	0 014	0.01598	0.057	0.00701
H_2 molecule	0.05082	0.087	0.06438	0.18	0.01356
	KCl crystal				
H atom	0 00419	0 005	0 00990	0 028	0 00571
H_2 molecule	0.02990	0.052	0.04756	0.126	0 01766

The activation energy of H atom diffusion in NaCl crystals comes out to be 0·19 ev, though there is no experimental data to compare this value, according to Lidiard & Norgett (1972) self interstitial ions and atom (H centres) moved with activation energies less than 0·3 ev. The activation energy of Helium diffusion in KCl was shown by Wayne (1973) to be 0·39 ev. The diameter of H_2 emolecule is smaller than that of Helium. According to our calculation, it will be more than 0·47 ev. Thus it seems though our values agree with other calculations, our values might be a bit higher. This is due to the fact that in our calculation, we have relaxed ions in the first neighbouring shells whereas Fayne (1973) had relaxed ions in the first five nearest neighbouring shells. As pointed out by Borget & Lidiard (1968), as more and more ions are allowed to relax, the calculated activation energy diminishes.

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